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protective materials, intended to coat or bind the silicone anti-foam. The theory is that encapsulation, or binding, counteracts the unwanted spreading of the silicone oil of the anti-foam onto the surrounding detergent powder which spreading results in the reduction of the concentration of one of the most important ingredients of the foam control agents and, in extreme cases, depleting the foam control agent of the silicone oil altogether, thus deactivating the foam control agent. Encapsulating or protective materials are often used in combination with the carrier material.

Proposed binder or encapsulant material have been described in the art and include an organic material which is water soluble or water dispersible, substantially non-surface active and detergent impermeable, for example gelatin, agar and reaction products or tallow alcohol and ethylene oxide. Alternatively there is suggested the use of a water insoluble wax having a melting point in the range from 55° to 100° C. and a water insoluble emulsifying agent, a non-ionic surfactant, e.g. ethoxylated aliphatic C₁₂₋₂₀ alcohols with 4 to 20 oxyethylene groups, ethoxylated alkylphenols, fatty acids, amides of fatty acids, thio alcohols and diols, all having 4 to 20 carbon atoms in the hydrophobic part and 5 to 15 oxyethylene groups, a water soluble or water dispersible organic carrier comprising from 1 to 100% of a first organic carrier component having a melting point of from 38° to 90° C. and from 0 to 99% of a second organic carrier which is selected from ethoxylated non-ionic surfactants having a HLB of from 9.5 to 13.5 and a melting point from 5° to 36° C. Examples of the organic carrier materials include tallow alcohol ethoxylates, fatty acid esters and amides and polyvinylpyrrolidone. There is also described the use of a material which is impervious to oily anti-foam active substance when in the dry state yet capable of disruption on contact with water, e.g. materials with a waxy nature, which may form an interrupted coating that will allow water to pass through under was conditions or water soluble sugars.

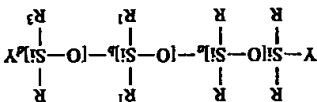
Many of the proposed binders and encapsulants are satisfactory in many situations. However, there is a continuing search for improved foam control agents, especially agents which will give improved powder characteristics.

We have now found that if the silicone anti-foam is absorbed on a zeolite carrier in combination with an organopolysiloxane copolymer and a polycarbonate-type binder or encapsulant, an improved silicone foam control agent is obtained which has better powder characteristics and has a better release of anti-foam in the early part of the washing cycle.

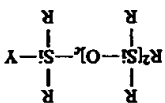
The invention provides in a first aspect a particulate foam control agent, comprising from 1 to 30 parts by weight of a silicone anti-foam, from 70 to 99 parts by weight of a zeolite carrier for the anti-foam, from 1 to 30 by weight of the silicone anti-foam, which has been deposited onto the zeolite carrier not later than the silicone anti-foam and from 1 to 40 parts by weight of a polycarbonate-type binder.

Silicone anti-foams for use in the foam control agents according to the invention are known materials and have been described in a number of patent specifications, including those referred to herein. Silicone anti-foams are foam regulating compositions which comprise a liquid organopolysiloxane polymer and a filler particle the surface of which has been rendered hydrophobic.

Liquid organopolysiloxane polymers which are useful in silicone anti-foams are also known and have been described in many patent specifications. Full description of all options is therefore not included but can be found in the many publications including patent application R.P. 578 424. Preferably they are linear or branched polymers having a structure according to the general formula



In formula (I) R denotes a monovalent hydrocarbon group having from 1 to 8 carbon atoms, preferably from 1 to 4 carbon atoms, R¹ denotes a group R, a hydroxyl group or a group



wherein R² denotes a divalent hydrocarbon, hydrocarbon-oxy or siloxane group or oxygen, R³ denotes a C₃₋₃₅ alkyl group, Y denotes a group R or a hydroxyl group, a, b, c and d have a value of 0 or an integer, provided at least one of a and b is an integer, and the total of a+b+c+d has a value such that the viscosity of the organopolysiloxane polymer at 25° C. is at least 50 mm²/s, preferably at least 500 mm²/s. The linear organopolysiloxanes may be linear, in which case R¹ denotes R or a hydroxyl group. It is preferred for the linear organopolysiloxanes that Y denotes a group R and that b=0. More preferred are those linear polymers wherein d=0 and wherein at least 80% of all R groups denote an alkyl group having from 1 to 4 carbon atoms, most preferably methyl. It is most preferred that the linear organopolysiloxanes are trimethylsiloxane end-blocked polydimethylsiloxanes. The preferred viscosity of the linear organopolysiloxanes is from 500 to 100,000 mm²/s, more preferably 1000 to 60,000 mm²/s at 25° C.

Organopolysiloxanes which are not linear are also known in the art. The preferred non-linear materials are those having branching in the siloxane chain. These polymers have a structure according to Formula (II), wherein b has a value of at least 1 and R² is preferably a divalent siloxane group or an oxygen atom. Particularly preferred siloxane groups R² are small three-dimensional siloxane resin particles which may have a number of pending siloxane polymer units. Branched siloxanes are known and examples of them have been described, together with a method of making them, in a number of patent specifications, e.g. G.B. 639 673, R.P. 31 532, R.P. 217 501, R.P. 273 448, DE 38 05 661 and G.B. 2 257 709.

Preferred liquid organopolysiloxanes are branched or higher viscosity siloxanes, i.e. above 12,500 mm²/s at 25° C.), especially the branched siloxanes, as they show an improved ability to control foam in most aqueous surfactant solutions.

Filler particles which are useful in the anti-foams for use in foam control agents according to the present invention are also well known and have been described in many publications. They are finely divided particulate materials including silica, fumed TiO₂, Al₂O₃, zinc oxide, magnesium oxide, salts of aliphatic carboxylic acids, reaction products of isocyanates with certain materials, e.g. cyclohexylamine, alkyl amides, for example ethylene or methylene bis stearate. Most preferred are silica particles with a surface area

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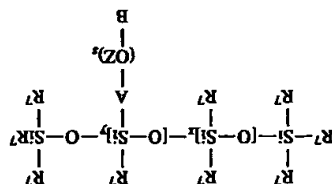
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DB=USPT; PLUR=YES; OP=OR

<u>L6</u>	(elastomer or rubber)[ab,ti,clm] and (tackifier or tackifying) and (phenolic adj resin)[ab,ti,clm] and (methylo same phenolic) and adhesive	7	<u>L6</u>
<u>L5</u>	(elastomer or rubber)[ab,ti,clm] and (tackifier or tackifying) and (phenolic adj resin) and (methylo same phenolic) and adhesive	17	<u>L5</u>
<u>L4</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj resin) and (methylo same phenolic) and adhesive	26	<u>L4</u>
<u>L3</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj resin) and (methylo same phenolic)	32	<u>L3</u>
<u>L2</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj rein)	1	<u>L2</u>
<u>L1</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj rein) and (methylo same phenolic)	0	<u>L1</u>

END OF SEARCH HISTORY

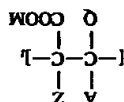


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cols (allyl-polyoxyalkylene polymers) in the presence of a noble metal catalyst. A hydrosilylation reaction will ensure the addition reaction of the allyl group to the silicon atom to which the hydrogen atom was bonded.

The binder or encapsulant is a polycarboxylate material. So-called polycarboxylate materials have been described in the art, and have the advantage that, as zeolites, they are useful ingredients in detergent compositions. Some of them have been suggested as polymeric coatings for antifoam ingredients in E.P. 484 081, in conjunction with a silicone oil antifoam and a solid carrier which, though suggested as possibly being a zeolite, is preferably a carbonate. No examples of the combination with zeolites is given, relating the arguments given above, relating to the release problems experienced with the use of zeolites as carriers without the use of this invention.

Polycarboxylate materials are known as dispersing agents in detergent powders and are water soluble polymers, copolymers or salts thereof. They have at least 60% by weight of segments with the general formula



wherein A, Q and Z are each selected from the group consisting of hydrogen, methyl, carboxymethyl, hydroxy and hydroxymethyl, M is hydrogen, alkali metal, ammonium or substituted ammonium and t is from 30 to 400. Preferably A is hydrogen or hydroxy, Q is hydrogen or carboxy and Z is hydrogen. Suitable polymers of unsaturated monomeric acids, e.g. acrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylcitraconic acid. The copolymerisation with lesser amounts of monomeric maleic acid, citraconic acid and methylcitraconic acid. The copolymers comprising no carboxylic acid, e.g. vinylmethyl, vinylmethyl, styrene and ethylene is not detrimental to the use of the polycarboxylates in the foam control agents of the present invention. Depending on the type of polycarboxylate this level can be kept low, or levels can be up to about 40% by weight of the total polymer or copolymer.

Particularly suitable polymeric polycarboxylates are polyacrylates with an average viscosity at 23° C. in mPa.s from 50 to 10,000, preferably 2,000 to 8,000. The most preferred polycarboxylate polymers are acrylate/maleate or acrylate/fumarate copolymers or their sodium salts. Molar mass of suitable polycarboxylates may be in the range from 1,000 to 500,000, preferably 3,000 to 100,000, most preferably 15,000 to 80,000. The ratio of acrylate to maleate or fumarate segments of from 30:1 to 2:1. Carboxylates may be supplied in powder form or liquid forms. They may be liquid at room temperature or may be supplied as aqueous solutions. The latter are preferred as they facilitate the manufacture of the foam control agents according to the invention with conventional spray applications. Many of the polycarboxylates are hygroscopic but are claimed not to absorb water from the air when formulated in detergent powders. It was surprisingly found that the use of polycarboxylates as binders and/or encapsulants for antifoam in the foam control agents of the present invention enabled a more efficient absorption of antifoam onto the carrier, resulting in the combination of all the ingredients allowed the manufacture of a particulate foam control agent with improved powder characteristics. For example, foam control agents according to the invention provide better mechanical

R⁷ in these more preferred copolymers may denote any alkyl or aryl group having up to 18 carbon atoms, more preferably 6. Particularly preferred are methyl, ethyl or phenyl groups. Especially preferred are those copolymers wherein at least 80% of all R⁷ groups in the copolymer, most preferably substantially all R⁷ groups, are methyl groups. A in these more preferred copolymers denotes a C₂₋₃ alkylene unit, most preferably propylene or isopropylene. Z preferably denotes a dimethylene group for at least half of all Z groups present in the copolymer, the other half being isopropylene groups. More preferably at least 70% of all Z groups are dimethylene groups, most preferably all Z groups, making the polyoxyalkylene portion a polyoxyethylene portion. B preferably denotes a hydroxyl group or an acyl group. The value of x may be 0 or an integer, preferably from 1 to 500, and the value of y may be any integer, preferably a value of from 1 to 500. x, y and s are chosen thus that the copolymer is either fully soluble or is dispersible in water or preferably in an aqueous surfactant solution. It is therefore preferred to balance the hydrophobic nature of the copolymer, which is determined to a large extent by the value of x, with the hydrophilic nature, which is determined to a large extent by the value of y and s and by group Z. E.g. if the value of x is large, a long siloxane chain is formed which will make the copolymer less soluble and more dispersible in the aqueous surfactant solution of the washing liquor. This may be balanced by increasing the amount of units having oxyalkylene groups (value of y) and by the size of the polyoxyalkylene groups (value of s), especially where Z is dimethylene). Particularly preferred organopolysiloxane polyoxyalkylene copolymers will be those where the value of x+y is in the range of from 1 to 500. A first more preferred copolymer has a value for x+y in the range from 1 to 50. The preferred ratio for these materials of y/x+y is from 0.02 to 1, more preferably 0.08 to 1. The value of s is preferably in the range from 4 to 60, more preferably 5 to 40, most preferably 7 to 36. A particularly useful copolymer is the one wherein x+y has a value of about 1 to 20, y/x+y has a value of about 0.3 to 1 and s has a value of 12, wherein the majority of Z units are dimethylene units. A second more preferred copolymer has a value for x+y in the range from 50 to 500, even more preferably 80 to 350. The preferred ratio for these materials of y/x+y is from 0.02 to 0.1, more preferably 0.05 to 0.08. The value of s is preferably as for the first more preferred copolymer. A particularly useful way of making suitable copolymers is by reaction of organopolysiloxanes having silicon-bonded hydrogen atoms with appropriate allyl-

units.

the Z units are dimethylene units and half are isopropylene

value of about 0.09 and s has a value of 36, wherein half of

wherein x+y has a value of about 100 to 120, y/x+y has a

copolymer. A particularly useful copolymer is the one

The value of s is preferably as for the first more preferred

of y/x+y is from 0.02 to 0.1, more preferably 0.05 to 0.08.

preferably 80 to 350. The preferred ratio for these materials

has a value for x+y in the range from 50 to 500, even more

are dimethylene units. A second more preferred copolymer

to 1 and s has a value of 12, wherein the majority of Z units

has a value of about 1 to 20, y/x+y has a value of about 0.3

36. A particularly useful copolymer is the one wherein x+y

from 4 to 60, more preferably 5 to 40, most preferably 7 to

preferably 0.08 to 1. The value of s is preferably in the range

ratio for these materials of y/x+y is from 0.02 to 1, more

has a value for x+y in the range from 1 to 50. The preferred

the range of from 1 to 500. A first more preferred copolymer

ene copolymers will be those where the value of x+y is in

Particularly preferred organopolysiloxane polyoxyalky-

lene groups (value of y) and by the size of the polyoxyalky-

lene groups (value of s), especially where Z is dimethylene).

balanced by increasing the amount of units having oxyalky-

copolymer less soluble and more dispersible in the aqueous

surfactant solution of the washing liquor. This may be

balanced by increasing the amount of units having oxyalky-

lene groups (value of y) and by the size of the polyoxyalky-

lene groups (value of s), especially where Z is dimethylene).

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surfactant solution of the washing liquor. This may be

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lene groups (value of s), especially where Z is dimethylene).

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balanced by increasing the amount of units having oxyalky-

lene groups (value of y) and by the size of the polyoxyalky-

lene groups (value of s), especially where Z is dimethylene).

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*DB=USPT; PLUR=YES; OP=OR***Hit Count Set Name**

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<u>L10</u>	L9 not l6	2	<u>L10</u>
<u>L9</u>	(elastomer or rubber) same (tackifier or tackifying) same (phenolic adj resin) same (methylo same phenolic)	2	<u>L9</u>
<u>L8</u>	(elastomer or rubber) same (tackifier or tackifying) and (phenolic adj resin) same (methylo same phenolic)	23	<u>L8</u>
<u>L7</u>	(elastomer or rubber)[ab,ti,clm] and (tackifier or tackifying) and (phenolic adj resin)[ab,ti,clm] and (methylo same phenolic)	10	<u>L7</u>
<u>L6</u>	(elastomer or rubber)[ab,ti,clm] and (tackifier or tackifying) and (phenolic adj resin)[ab,ti,clm] and (methylo same phenolic) and adhesive	7	<u>L6</u>
<u>L5</u>	(elastomer or rubber)[ab,ti,clm] and (tackifier or tackifying) and (phenolic adj resin) and (methylo same phenolic) and adhesive	17	<u>L5</u>
<u>L4</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj resin) and (methylo same phenolic) and adhesive	26	<u>L4</u>
<u>L3</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj resin) and (methylo same phenolic)	32	<u>L3</u>
<u>L2</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj rein)	1	<u>L2</u>
<u>L1</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj rein) and (methylo same phenolic)	0	<u>L1</u>

END OF SEARCH HISTORY



US005589449A

United States Patent [19]
Kolaitis et al.
Patent Number: 5,589,449
Date of Patent: Dec. 31, 1996 [45]

[54] PARTICULATE FOAM CONTROL AGENTS

[75] Inventors: Leonidas Kolaitis, Meise; Bertrand L. J. Lenoble, Bois-de-Lessines; Mark A. Prince, Overijse, all of Belgium

[73] Assignee: Dow Corning S.A., Senefte, Belgium

[21] Appl. No.: 279,755

[22] Filed: Jul. 22, 1994

[30] Foreign Application Priority Data

Jul. 29, 1993 [GB] United Kingdom 9315675
Jan. 14, 1994 [GB] United Kingdom 9400599

[51] Int. Cl.⁶ B01D 19/04; C10D 3/20
[52] U.S. Cl. 510/466; 252/321; 252/358;
510/358; 510/361; 510/377; 510/507

[58] Field of Search 252/321, 358,
252/174.15; 510/466

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[57] ABSTRACT

A particulate foam control agent comprises 1 to 30 parts silicone antifoam, 70 to 99 parts zeolite carrier, 1 to 60% of the antifoam of an organopolysiloxane polyoxyalkylene copolymer, deposited onto the zeolite carrier not later than the antifoam and 1 to 40 parts by weight of a polycarboxy-late-type binder or encapsulant. This combination give good release in early stages, storage stability and powder charac-teristics.

19 Claims, No Drawings

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2257709 7/1992 United Kingdom
C10D 3/37
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C10D 3/37
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C10D 3/08

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<u>L9</u>	(elastomer or rubber) same (tackifier or tackifying) same (phenolic adj resin) same (methylol same phenolic)	2	<u>L9</u>
<u>L8</u>	(elastomer or rubber) same (tackifier or tackifying) and (phenolic adj resin) same (methylol same phenolic)	23	<u>L8</u>
<u>L7</u>	(elastomer or rubber)[ab,ti,clm] and (tackifier or tackifying) and (phenolic adj resin)[ab,ti,clm] and (methylol same phenolic)	10	<u>L7</u>
<u>L6</u>	(elastomer or rubber)[ab,ti,clm] and (tackifier or tackifying) and (phenolic adj resin)[ab,ti,clm] and (methylol same phenolic) and adhesive	7	<u>L6</u>
<u>L5</u>	(elastomer or rubber)[ab,ti,clm] and (tackifier or tackifying) and (phenolic adj resin) and (methylol same phenolic) and adhesive	17	<u>L5</u>
<u>L4</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj resin) and (methylol same phenolic) and adhesive	26	<u>L4</u>
<u>L3</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj resin) and (methylol same phenolic)	32	<u>L3</u>
<u>L2</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj rein)	1	<u>L2</u>
<u>L1</u>	(elastomer or rubber) and (tackifier or tackifying) and (phenolic adj rein) and (methylol same phenolic)	0	<u>L1</u>

END OF SEARCH HISTORY

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16

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IES VISUAL COMFORT PROBABILITY

RATED LUMENS PER LAMP 2900

100 FC. RELECTANCE 80/50/20

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30	40	84	80	74	68	92	89	87	83
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40	40	87	83	77	70	93	91	88	82
40	60	87	84	78	72	94	91	89	84
40	80	88	85	80	74	94	92	90	85
40	100	89	86	81	76	94	92	90	86
60	30	88	84	78	74	93	91	88	82
60	40	89	85	79	73	94	92	89	83
60	60	89	86	80	75	94	92	90	84
60	80	89	87	82	76	95	92	90	85
60	100	90	87	82	78	95	93	91	86
100	40	91	88	83	78	95	93	91	86
100	50	91	89	84	79	95	94	91	87